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UNSATURATED SULTONE DERIVATIVES OF PROTEINS

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This invention relates to methods of chemically modifying proteinaceous materials and to the resulting compositions. More specifically, the invention concerns reaction products of proteinaceous materials and internal esters of sulfonic acids and to the products produced by the polymerization of proteins which have been modified by treatment with unsaturated internal esters of sulfonic acid. The invention is based, in part, on the initial discovery that proteins may be chemically modified by reaction with alkane and alkene sultones to produce products having substantially different characteristics from the unmodified materials.

Historically, workers in the field have attempted for several years to find a commercially practicable method for coupling proteinaceous materials. Numerous chemical cross-linking agents such as aldehydes, polyamines, polycarboxylic acids, acid anhydrides, etc., have been investigated. In almost every instance in which coupling occurred, the disadvantages far outweighed the advantages. For example, attempts to chemically modify proteins ordinarily meet with difficulty in that loss of inherent desirable qualities, such as high molecular weight, tensile strength, solubility, etc., often result due to the necessary reaction conditions or components which may lead to denaturation, hydrolysis, etc. Other disadvantages include insolubility in suitable solvents, the inability to control the reaction or stop it at a desired point, and the production of heterogeneous products that do not lend themselves to formation of continuous films.

Therefore, it is an object of this invention to produce new and useful compositions utilizing proteinaceous materials.

A further object of the invention is the provision of an improved method for upgrading proteinaceous materials to provide valuable new industrial products.

Another object is to provide a means whereby water solubilizing groups can be introduced into a protein structure under very mild conditions.

An additional object is to provide modified proteinaceous material which can be subsequently polymerized.

A further object is to produce proteinaceous materials which are soluble in suitable solvents and which produce a homogeneous product which lends itself to the formation of continuous films.

Other objects and advantages will become apparent to those skilled in the art from the detailed description which follows.

Generally, the invention is concerned with the treatment of proteins and hydrolytic degradation products of proteins to form valuable products which have significantly decreased isoelectric points, increased water solubilities and are more readily alkali dispersible. In one embodiment of the invention, sulfoalkenyl groups are attached to one or more amino, hydroxy, mercapto, imino groups of the proteinaceous substance resulting in a vinyl-type molecule. The anchoring of such vinyl groups to the proteinaceous residue permits polymerization to very large molecular weight materials which retain their solubility in water or dilute alkali due to the multiplicity of sulfonic acid functions. On the other hand, depending upon the vinyl monomers and/or amounts utilized, water insoluble copolymers

are possible. Homopolymers as well as copolymers with vinyl monomers result in typical resin emulsions which exhibit considerable adhesive properties. These emulsions can be dried to reasonably clear films and yield clear, viscous solutions when dissolved in dimethyl formamide, n-methyl pyrrolidone or methyl butynol. As used herein, the term "protein" or "proteinaceous substance" is intended to include the hydrolytic degradation products of proteins.

More specifically, the modified proteins of this invention are prepared by the treatment of a solvent solution or suspension of protein, under mild alkaline condition, with a sultone so as to condense the sultone with the protein molecule. Generally speaking, the reaction is carried out for at least about one hour at a temperature of about 40° C. to 50° C. and at a pH of about 8 to 10. These moderately mild reaction conditions are preferred because of a desire to maintain hydroyltic breakdown to a minimum. However, more strenuous conditions of temperature and alkalinity are practicable and sometimes even useful. For example, resistant keratin protein may be "sultonated" advantageously at temperature above 60° C. On the other hand, nongelling proteins such as casein, soy or albumens may react at 20° C. albeit more slowly. The sulfoalkenyl modified protein can be polymerized with vinyl monomers by means of the conventional vinyl-type catalyst. Generally, the temperature at which the polymerization reaction is carried out will depend upon the monomers employed and also the modified protein. Temperatures of about 20° to 150° C. are contemplated, however, a temperature in the range of 80–90° C. insures a reasonable reaction time of around ½ to 2 hours for completion of the reaction.

Protein materials with which the sultones react include all proteinaceous substance which can be placed in a dispersion or solution on the alkaline side. They include animal and vegetable proteins of both the simple and conjugated type. Nonlimiting examples are soybean, zein, cottonseed, peanut, casein of the alkaline soluble group, as well as their seed meals and hydrolysis products. A second group includes the keratins, including hoof, horn, wool, and feathers. A third group comprises casein, collagen, glue, gelatin and hydrolysis products such as stick which is the evaporated hydrolysis water obtained from wet or steam rendering. All proteinaceous materials or their derivatives that are aqueous or alcohol-aqueous soluble are preferred; however, proteins which are dispersible in other solvents are usable. Such solvents include N-methyl pyrrolidone, dimethyl sulfoxide, dimethyl formamide, and methyl butynol. The protein may be in the native, denatured or degraded state through hydrolysis, such as in the form of polypeptides.

In the preparation of protein derivatives by reaction with the sultones numerous procedures may be used other than the conventional dispersion of the sultone into a mildly alkaline aqueous solution of the protein.

(a) The protein solution may be diluted with methanol or ethanol to the point of incipient precipitation of the protein and then treated with an alcoholic solution of the sultone.
(b) The procedure of (a) can be followed using acetone in place of the alcohols.
(c) Either dimethyl formamide, dimethyl sulfoxide, or N-methyl pyrrolidone may be used as partial solvents with water for this reaction.

Irrespective of the method used, we have found that reaction is most rapid when the protein is in solution. If not, then very finely divided material, similar to spray dried gelatin or albumen is preferred.

Suitable starting materials for the process according to the present invention are the gamma sultones, i.e., 3-hy-